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Enhanced Hydrogen Production Integrated with CO_2 Separation in a Single-Stage Reactor

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ABSTRACT

Hydrogen production from coal gasification can be enhanced by driving the equilibrium limited Water Gas Shift reaction forward by incessantly removing the CO_2 by-product via the carbonation of calcium oxide. This project aims at using the OSU patented high-reactivity mesoporous precipitated calcium carbonate sorbent for removing the CO_2 product. Preliminary experiments demonstrate the show the superior performance of the PCC sorbent over other naturally occurring calcium sorbents. Gas composition analyses show the formation of 100% pure hydrogen. Novel calcination techniques could lead to smaller reactor footprint and single-stage reactors that can achieve maximum theoretical H_2 production for multicyclic applications. Sub-atmospheric calcination studies reveal the effect of vacuum level, diluent gas flow rate, thermal properties of the diluent gas and the sorbent loading on the calcination kinetics which play an important role on the sorbent morphology. Steam, which can be easily separated from CO_2, is envisioned to be a potential diluent gas due to its enhanced thermal properties. Steam calcination studies at 700-850 ^oC reveal improved sorbent morphology over regular nitrogen calcination. A mixture of 80% steam and 20% CO_2 at ambient pressure was used to calcine the spent sorbent at 820 ^oC thus lowering the calcination temperature. Regeneration of calcium sulfide to calcium carbonate was achieved by carbonating the calcium sulfide slurry by bubbling CO_2 gas at room temperature.

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EXECUTIVE SUMMARY

Hydrogen production from coal gasification can be enhanced by driving the equilibrium limited Water Gas Shift reaction forward. This is achieved by incessantly removing the CO_2 by-product via the carbonation of calcium oxide. This project aims at using the OSU patented high-reactivity mesoporous precipitated calcium carbonate sorbent for removing the CO_2 product. This augments the hydrogen yield, purity and enables high CO conversions while enabling stoichiometric steam requirements. Besides, this process generates a pure sequestration-ready CO_2 stream leading to effective carbon management strategies. The combined WGS and carbonation were conducted at 600 ^oC with a steam to carbon monoxide ratio of ratio of 3:1. These preliminary experiments demonstrate the superior performance of the PCC sorbent over other naturally occurring calcium sorbents such as Linwood Carbonate (LC) and Linwood Hydrate (LH) as demonstrated by the breakthrough curves obtained from CO conversions. Gas composition analyses show the formation of 100% pure hydrogen. In addition, the product gas composition analyses (CO_2 and H_2) reveal the superior performance of the PCC sorbent over other commercial sorbents. Gas composition analyses (steam and N_2 free) show the formation of 100% pure hydrogen during the first 139 seconds for the PCC-HTS system.

The success of this process depends on the regenerability of the sorbent for multiple cycles of WGS-carbonation and calcination. Novel calcination techniques could lead to smaller reactor footprint and single-stage reactors that can achieve maximum theoretical H_2 production for multicyclic applications. Two types of limestone calcinations: sub-atmospheric and steam calcinations were investigated. Detailed thermodynamic analyses reveal the need for high temperatures (above 890 ^oC) for calcination at atmospheric pressures. High temperature is known to cause sorbent sintering which is a major cause for loss in reactivity. However, by operating under lower CO_2 partial pressures we can decrease the calcination temperature below 890 ^oC, as calculated by thermodynamic curves, thus preventing the high temperature sintering effects. Thus, we have identified sub-atmospheric calcination (vacuum) as vital regeneration technique that can help preserve the sorbent morphology. Sub-atmospheric calcination studies reveal the effect of vacuum level, diluent gas flow rate, thermal properties of the diluent gas and the sorbent loading on the calcination kinetics which play an important role on the sorbent morphology. Lowering vacuum levels, reducing sorbent loading and increasing diluent gas flow rates augments the calcination rate and the mass/heat transfer rates. Diluent gas flows during calcination augments the necessary convective heat transfer rate which is directly related to the diluent gas flow rate. This results in improved calcination kinetics and sorbent morphology. Diluent gas thermal properties like thermal conductivity and specific heat capacity play a significant role on the heat transfer rates during calcination.

The other technique to lower the CO_2 partial pressure is by using a diluent gas to calcine the sorbent. Steam, which can be easily separated from CO_2, is envisioned to be a potential diluent gas due to its enhanced thermal properties. Steam calcination studies at 700-850 ^oC reveal improved sorbent morphology over regular nitrogen calcination. Calcination at lower temperatures demonstrates improved sorbent reactivity due to reduced sorbent sintering effects. A mixture of 80% steam and 20% CO_2 at ambient pressure was used to calcine the spent sorbent at 820 ^oC thus lowering the calcination temperature by reducing the CO_2 partial

pressure. However, the reactivity of the steam-calcined sorbent is poor compared to the N_2 calcined samples.

The synthesis gas produced during coal gasification contains sulfur impurities in the form of hydrogen sulfide, which reacts with the calcium sorbent to form calcium sulfide. Disposal of calcium sulfide involves either oxidizing it to calcium sulfate or other treatments which include converting it to calcium carbonate. Regeneration of calcium sulfide to calcium carbonate was achieved by carbonating the calcium sulfide slurry by bubbling CO_2 gas at room temperature as revealed by x-ray diffraction analysis. Addition of anionic dispersant (N40V) to the calcium sulfide slurry, during the calcium sulfide regeneration process, improves the resultant calcium carbonate sorbent morphology which is corroborated by increase in pore volume. This results in improved sorbent reactivity toward CO_2 capture.

INTRODUCTION

The foreseeable enhanced use of gasification systems is based upon their higher energy to electricity efficiency, ability to convert fossil fuel energy to hydrogen, and an envisaged ease of carbon management thereby increasing their importance in a carbon constrained world. Numerous agencies are promoting the use of coal, which occurs abundantly, in gasification systems to aid hydrogen production for the envisaged hydrogen economy and to enhance domestic energy security. The water gas shift reaction (WGSR) plays a major role in increasing the hydrogen production from fossil fuels. However, the enhanced hydrogen production is limited by thermodynamic constraint posed by the equilibrium limitation of the WGSR. However, this constraint can be overcome by concurrent water-gas shift (WGS) and carbonation reactions to enhance H_2 production by incessantly driving the equilibrium-limited WGSR forward and by in-situ CO_2 removal from the product gas mixture. This process can effectively and economically produce a pure H_2 stream by coal gasification with integrated capture of CO_2 emissions, for its subsequent sequestration. This project involves enhanced hydrogen production at high temperatures via the simultaneous carbonation and WGS reactions given below:

WGSR: $\mathbf{CO + H_2O <=> CO_2 + H_2}$ **(1)**

Carbonation Reaction: $\mathbf{CaO + CO_2 \rightarrow CaCO_3}$ **(2)**

The spent sorbent ($CaCO_3$) can then be calcined separately to yield a pure sequestration ready CO_2 stream, which is then amenable for compression and liquefaction before its transportation to sequestration sites. Calcination reaction, reverse of the carbonation reaction can be written as:

Calcination Reaction: $\mathbf{CaCO_3 \rightarrow CaO + CO_2}$ **(3)**

The resulting CaO sorbent is recycled to capture CO_2 in the next cycle. This cyclical CCR process can be continued as long as the sorbent provides a satisfactory CO_2 capture. However, for the sorbent to sustain its activity over multiple CCR cycles it needs to be calcined efficiently. High temperature causes sorbent sintering. This is especially crucial if calcination is carried out at ambient pressure because thermodynamic analyses predict very high temperatures (>900 ^{o}C) for calcination of the carbonate. Thus lowering the calcination temperature plays a key role in maintaining the sorbent reactivity over subsequent cycles.

Predominantly, two types of calcination processes are investigated for this purpose: sub-atmospheric calcination and steam calcination.

Sub-atmospheric (vacuum) calcination

It has been suggested in literature that CaO procured from the calcination of limestone under vacuum has a higher reactivity. Beruto and Searcy (1976) observed that, under air calcination at 650 - 800 ^{o}C, sharp edges of calcite powder were replaced by rounded surfaces and neck areas indicating severe sintering. The resulting CaO structure was highly crystalline as well. In contrast, the sharp edges of calcite were retained in the CaO obtained under vacuum. However, the CaO did not possess a high degree of crystallinity. The latter also showed high reactivity towards hydration. Dash et al., (2000) also observed a metastable-nanocrystalline calcia under vacuum and stable microcrystalline when calcined in helium. Beruto et al., (1980) estimated the surface area and pore volume of limestone based CaO to be about 78-89 m^2/g and 0.269 ml/g respectively. However, this calcination occurred at 550^{o}C under very high vacuum levels (aided by diffusion pumps) and the calcination took about a week to complete. While it is beneficial to observe a high SA and PV in the resulting CaO sorbent, such a calcination procedure is both time consuming and very expensive. A practical calcination technique that optimizes kinetics and sorbent morphology while attaining CO_2 separation goals needs to be developed.

Ingram and Marrier (1963) reported that the rate of reaction varies linearly with the difference between equilibrium partial pressure and the partial pressure of CO_2 surrounding the solid. This further supports the need for sub-atmospheric calcination that continuously removes CO_2 as it is formed around the calcining $CaCO_3$ particles. Experimentally, Kelley & Anderson (1935) demonstrated the onset of calcination at 640 ^{o}C, which would be the lower temperature bound for the CCR process under consideration. Thus the role of calcination temperature, level of vacuum, thermal properties of diluent gas and the effect of diluent flow on the kinetics of calcination and the morphology of the resultant CaO sorbent are investigated in this study.

Steam Calcination

In our previous investigation (March 2005 report) we had reported our investigation with sub-atmospheric or vacuum calcination procedures. However, the cost associated with the use of vacuum can be a limiting factor in implementing this step. Hence, the focus is to use steam to calcine the spent sorbent.

It has been widely observed that steam calcination of $CaCO_3$ occurs at a faster rate. Berger (1927) investigated the effects of steam calcination of a commercial Bellefonte, Pa., limestone ($CaCO_3$) at various temperatures ranging from 600 – 1000 ^oC and compared the rate of calcination with that obtained under an inert gas (Helium) atmosphere and in air. The rate of calcination at any given temperature was greater in steam than in air, while it was comparable to that in helium. At 800 ^oC, steam calcination was 30% faster than air calcination due to the difference in thermal properties between steam and air. Further, the CaO resulting from steam calcination exhibited higher rates of slaking, indicating a higher reactivity product compared to the CaO obtained from air calcination. Chemical or mechanical action of steam to enhance the rate of calcination was not taken into consideration. The enhanced calcination was attributed to the superior heat transfer properties of steam (higher thermal conductivity and heat capacity) as compared to that of air or nitrogen.

MacIntire and Stansel (1953) reported the calcination of high-calcitic limestone fines with steam over a temperature range of 600 - 900 ^oC. They obtained complete calcinations (100 %) at a temperature of 700 ^oC, whereas under the same temperature conditions air resulted in only 1.6 % calcination. They came to the conclusion that steam injection into the limestone was necessary to accelerate complete calcination. At most, the conversion of limestone fines at 700ºC in steam represented a decrease of 210ºC from the recognized critical for the calcination of limestone in air. Above 700ºC, the decrease does not register as large of a difference. Separation of CO_2 was also achieved by condensing out the steam in the mixture by simply cooling the exit gases below the dew point of steam. In addition, Terry and McGurk (1994) postulated that steam calcination occurs rapidly due to catalytic effect of steam. Rate equations for steam-catalyzed decomposition of $CaCO_3$ based on the formation of an activated calcium bicarbonate intermediate species have been successful in matching the calcination data from numerous studies. The authors observed a 20% increase in

calcination rate in the presence of steam at 834 ^{o}C. Wang and Thompson (1995) hypothesized that the surface adsorption of H_2O weakens the CaO-CO_2 bond leading to an enhanced calcination rate. This study used dynamic XRD technique to conclude that a 0.77% steam in helium caused a 35% increase in the conversion compared to dry helium. The results show that at 0.0077 atm of steam, there is a significant enhancement of the decomposition rate. However, at steam pressures above 0.0077 atm, the decomposition rate of calcium carbonate is no longer a function of the steam partial pressure. Also, under conditions of the same environment, the rate of decomposition increases with temperature.

In this study we investigate the use of steam as a diluent gas to effect the calcination of the spent sorbent ($CaCO_3$). Finally, the use of steam enables the separation of CO_2 and steam by condensation of the used steam, leading to a pure CO_2 stream.

Regeneration of Calcium Sulfide

While hydrogen production from coal gasification seems economical, the sulfur present in coal leads to the formation of hydrogen sulfide (H_2S) under the reducing conditions in the gasifier. Downstream requirements imposed by the gas turbine and the purity standards of hydrogen for its use in chemical production and PEM fuel cell operation necessitate that the H_2S be reduced significantly. Based on the exact requirement, the concentration of H_2S could be as low as 10 ppm.

One of the processes that reduce H_2S involves its reaction with calcium-based sorbents such as CaO and $CaCO_3$ to form calcium sulfide (CaS) through a heterogeneous, high temperature gas solid reaction (Fenouil and Lynn, 1995[a,b]; Chauk et al., 2000). However CaS cannot be safely disposed as it can evolve H_2S gas or cause sulfide ions to leach into ground water. Hence, CaS needs additional chemical treatments to stabilize it. There are several approaches to handling CaS. In one scheme, high temperature reactions that completely convert CaS back to $CaCO_3$ can be employed by its reaction with steam and CO_2 (Adanez, et al., 2001). This reaction, carried out at 650^{o}C, can be written as:

$CaS + H_2O$ (steam) + $CO_2 \rightarrow CaCO_3 + H_2S$ **---- (4)**

This process provides a stream of H_2S as well as $CaCO_3$ that can be recycled back for additional H_2S removal in a subsequent cycle. However, this leads to a loss in sorbent reactivity after a few cycles of sulfidation regeneration reaction. The sulfidation extent of

$CaCO_3$ dropped from 69% in the first cycle to 13% at the end of 21 cycles (Keairns et al., 1974). Another process involves the high temperature oxidation (at 920^oC) of CaS to form $CaSO_4$, which is more amenable to land filling, as it is a stable and relatively unreactive compound (Qiu, et al., 1999). However, the formation of a larger molar volume product ($CaSO_4$) leads to pore pluggage and pore mouth closure, which limits the sorbent from attaining complete conversion. Hence it is possible that the sorbent always contained unconverted CaS, thereby making this oxidation procedure difficult to deploy in practice.

A different approach can be employed that converts CaS back to $CaCO_3$ in an aqueous phase. The regeneration of CaS can be carried out by bubbling CO_2 through aqueous slurry of CaS. The overall stoichiometric reaction can be written as:

$CaS + H_2O$ (water) + CO_2 → $CaCO_3 + H_2S$ ---(5)

This reaction, which occurs at ambient temperature, goes to completion and leads to the formation of H_2S. H_2S laden gas can be processed using conventional processes such as the Claus process to convert it to sulfur or sulfuric acid that can add revenue streams to the entire plant operations. Currently, a low temperature amine based process that separates H_2S from fuel gas originating from coal gasification does indeed create a revenue stream at the Tampa Electric's Polk Power Plant in Florida by selling sulfuric acid to the fertilizer industry in the vicinity. The use of a regenerative calcium based desulfurization process has additional advantages. For example, the use of calcium over multiple cycles drastically reduces the requirement of fresh calcium sorbent, as a majority of it is recycled. A related benefit is that the quantity of byproducts that require additional management such as land filling is also reduced.

A few studies have been reported in the literature on this reaction. Biswas et al. (1976) aimed at sulfur recovery from gypsum. Their studies on the aqueous phase carbonation of reduced gypsum confirmed that a high degree of conversion could be attained by this process. In fact less than 1% sulfur was left after the carbonation reaction. This reaction is hypothesized to occur in two steps:

$2CaS + H_2O + CO_2$ → $Ca(HS)_2 + CaCO_3$ ---- (6)

$Ca(HS)_2 + H_2O + CO_2$ → $2\ H_2S + CaCO_3$ ---- (7)

This aqueous phase reaction exhibits a sigmoidal conversion plot for increasing time. The reaction rate is slow in the beginning due to the limited solubility of CaS in water. However,

H_2S formed as a result of carbonation, starts reacting with the CaS itself, converting it to higher solubility $Ca(HS)_2$. Eventually the carbonation slows down due to the depletion of $Ca(HS)_2$ in the slurry.

Jia and Lu (1992) continued this work by attempting to derive rate constants for the carbonation of CaS. They observed a slight optimization in the extent of conversion at 60^{o}C. This optimization is a balance between enhanced reaction rates and a decrease in absorption of CO_2 in water and CaS solubility as the temperature increases. They estimated that the concentration of H_2S in the exit gases (0.13 to 0.96) is sufficient for a Claus process following this carbonation step. A higher solid CaS loading in the slurry hastened the reaction due to an inherent rise in temperature as the reaction proceeds.

Nishev and Pelovski (1993) detailed the effect of reaction temperature and P_{CO2} on the kinetics of carbonation of CaS. An increase in P_{CO2} increases the rate of the reaction as well as the conversion. A higher P_{CO2} leads to faster nucleation that leads to a less porous $CaCO_3$ sorbent. Internal diffusion control dominated the progress of the reaction as evidenced by the activation energy values in the 17-27 kJ/mol. It was also shown that a higher P_{CO2} lead to a higher value of activation energy and pre-exponential factor.

Brooks and Lynn (1997) investigated the recovery of calcium carbonate and hydrogen sulfide from spent calcium sorbents. They used a methyldiethanolamine (MDEA) mediated carbonation procedure that enhances the reaction rate by creating complexes with both CO_2 and H_2S. The reactions are:

$$\mathbf{MDEA.H_2S + CaS \rightarrow MDEA + Ca(HS)_2} \qquad \textbf{---- (8)}$$

$$\mathbf{MDEA.H_2CO_3 + MDEA + Ca(HS)_2 \rightarrow 2\ MDEA.\ H_2S + CaCO_3} \qquad \textbf{---- (9)}$$

In this project we are aiming to recover CaS to form H_2S and $CaCO_3$. This aqueous phase carbonation provides a method to completely regenerate calcium-based sorbents, which lose reactivity towards high temperature reactions that are carried out in a cyclic fashion. Further it is our aim to study the morphology of the $CaCO_3$ that is formed for its surface area and pore volume characteristics, which are crucial for sorbent reactivity. A prior study has already indicated the efficacy of OSU's patented mesoporous sorbent towards the extent of sulfidation compared to naturally occurring limestone (Chauk et al., 2000). The main aim of this portion of the project is to recreate the mesoporous Precipitated Calcium Carbonate (PCC) structure starting from CaS instead of the conventional $Ca(OH)_2$ stating material. This

CaS can be pure or it could be the product of sulfidation of CaO or $CaCO_3$. The subsequent sections detail our efforts in this direction to date.

EXPERIMENTAL

Sub-atmospheric calcination reactor design

Figure 1 illustrates the schematic details of the calciner system. A detailed description is provided in the previous Annual Technical Progress Report (September 2004). This diagram shows the 3-D layout of the reactor tube and the electric furnace surrounding it. It also illustrates the choice of the diluent gas among helium, nitrogen and argon that have been used in the experiments. The results using these gases are described later in this report.

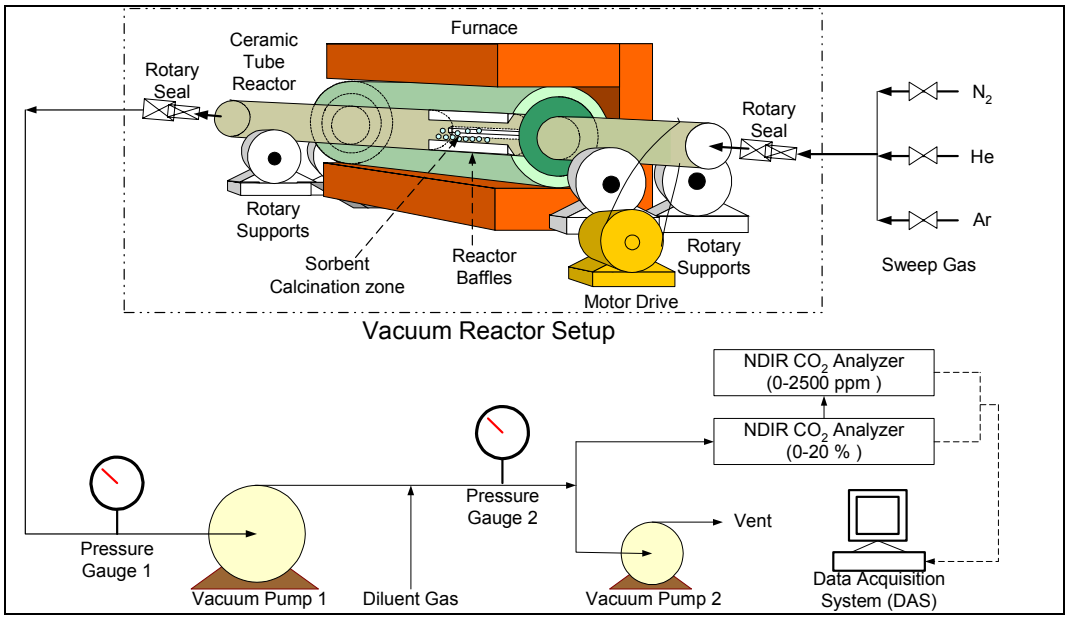


Figure 1: 3-D schematic diagram of the calciner reactor setup.

Modification WGS-Carbonation fixed bed Reactor Setup

From the previous experimental WGS-carbonation reactor setup, minor modifications were made to carry out multicyclic water gas shift reactions in the presence of CaO and catalyst. The modified reactor design assembly used to carry out these experiments is shown in Figure 2. The setup consists of a tube furnace, a steel tube reactor, a steam generating unit, a set of gas analyzers for the online monitoring of CO, CO_2, H_2, and steam concentrations, a condenser system to remove water from the exit gas stream and a high pressure water syringe pump. A significant change to the previous reactor configuration (described in Annual

Progress Report, September 2004) is the replacement of the modified variable area flowmeters with a set of five Brooks Instrument Model 5850E mass flow controllers which meter the gases up to an outlet pressure of 310 psig within an accuracy of 1%. In addition, the modified WGS reactor system now includes a single-pass countercurrent shell-tube heat exchanger as part of the steam condenser system. The coolant fluid is pure ethylene glycol entering the heat exchanger at –3°C. The coolant fluid is regulated at –3°C through a Julabo F25 Refrigerated and Heating Circulator. Two additional analyzers added to the new WGS reactor setup are the MAC Instruments MAC 120B Moisture Analyzer and an Applied Analytics H2A-528 Hydrogen Analyzer. The integration of these two instruments into the setup allows the H_2 and steam concentration to be accurately quantified in the outlet flow stream.

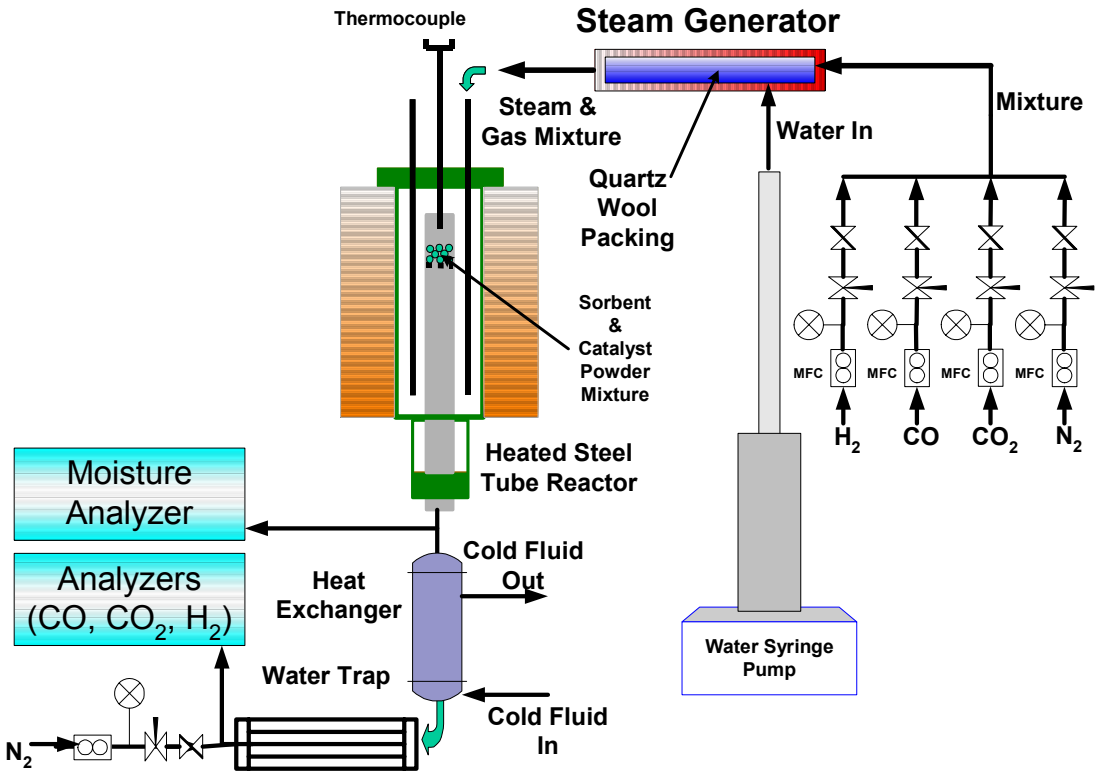


Figure 2. Modified reactor setup with for investigating WGS and carbonation reactions

Combined WGS-Carbonation Multi-Fixed Bed Reactor Design

Rationale for novel reactor design

We had performed simultaneous water gas shift and carbonation reactions in a fixed bed reactor using a catalyst-sorbent mixture. High temperature shift (HTS) catalyst (iron oxide supported on chromium oxide) was obtained from Süd-Chemie, Inc. OSU patented Precipitated calcium carbonate (PCC) and hydrated-lime from naturally occurring limestone (Linwood Hydrate, LH) were used as the precursors for the carbonation sorbents. The details of the investigation have been reported in the Annual Technical Progress report (September 2004). During the experiments, after the sorbent bed had achieved the initial breakthrough, the bed was regenerated by calcining the $CaCO_3$ formed in flowing N_2 at 700 ^oC. This regeneration was performed *in-situ* by heating the fixed bed containing sorbent-catalyst mixture concurrently. Subsequently, the catalyst-sorbent bed was subjected to a second WGSR-carbonation reaction cycle. However, the sorbent-catalyst bed depicted poor performance in the 2nd reaction cycle and the system was not even able to reach the sorbent-free (equilibrium) CO conversion of 81%. As a part of another study, the individual sorbents (without catalyst) had been subjected to numerous carbonation-calcination reaction cycles in a 10% CO_2 stream at 700 ^oC (Iyer et al, 2004). The sorbents depicted satisfactory performance without losing substantial reactivity over consecutive cycles as observed in this specific case. Thus, loss in this reactivity can be attributed to the loss in the catalyst activity after the 1st regeneration cycle. This is because the catalyst was subjected to CO_2, an oxidizing atmosphere, during the calcination phase. Thus, the deactivated catalyst was not able to catalyze the WGSR in the subsequent 2nd reaction phase resulting in poor CO conversion in the 2nd cycle.

These observations of catalyst deactivation are similar to those by Harrison and co-workers who report a single-step sorption-enhanced process to produce hydrogen from methane (Balasubramanian et al., 1999; Lopez-Ortiz and Harrison, 2001). They used the traditional concept of SMR with WGS using Ni-based catalyst to produce hydrogen, coupled with the novel scheme of *in-situ* continuous CO_2 capture using a calcium-based dolomite sorbent. However, they regenerated the dolomite sorbent in streams of N_2, 4%O_2 in N_2 and pure CO_2. They had to use high regeneration temperatures of 800-950 ^oC, especially while using pure CO_2. Exposure of the reforming catalyst to an oxidizing atmosphere (*viz.* O_2/N_2 or

CO_2) while regenerating the sorbent used to oxidize their Ni catalysts to NiO. Hence, their deactivated catalyst had to be reduced back to Ni before every cycle using hydrogen. This is evident from the fact that it took about 20 minutes for the H_2 concentration maximize.

Another alternative would be to separate the sorbent-catalyst mixture after every reaction phase such that only the sorbent is subjected to the regeneration conditions while the catalyst remain unaffected. In addition, calcination in a pure CO_2 stream will result in higher operating temperatures due to the thermodynamic limitations of the calcination reaction in presence of the CO_2 product. Higher temperatures and the presence of CO_2 during calcination would cause both the sorbent to sinter and the catalyst to deactivate. Hence, there is a need for a reactor design that prevents the catalyst from deactivation due to exposure to CO_2 product during calcination.

Envisaged novel Multi-Fixed Bed Reactor

The schematic illustration of the novel multi-fixed bed reactor is shown in Figure 3 below. The reactor consists of alternating fixed beds of HTS catalyst followed by CaO sorbent. During the reaction phase, the water gas reactant mixture, consisting of predominantly CO and H_2O enters one end of the reactor. Simultaneous WGSR and carbonation reactions occur, leading to enhanced hydrogen production. Finally, product gas, rich in hydrogen, leaves the other end of the reactor. Subsequently, in the regeneration phase, the two ends of the reactor are sealed and a diluent gas flow is introduced in between each of the three catalyst beds. Thus, there are three ports for introducing the diluent gas. In addition, vacuum will be introduced in between each of the sorbent beds as shown in the figure. These vacuum ports are strategically placed such that the applied vacuum will draw out the flowing diluent gas enabling calcination of the reacted sorbent. Besides, the CO_2 formed during the calcination process should flow out through these vacuum ports preventing the contact between the catalyst bed and CO_2. Besides, the use of sub-atmospheric calcination should lower the calcination temperature. Thus, we envision the sustenance of the catalyst activity and the sorbent reactivity. Nitrogen will be used as the diluent gas during initial testing phase. Future alternatives include the use of steam or steam/CO_2 mixtures.

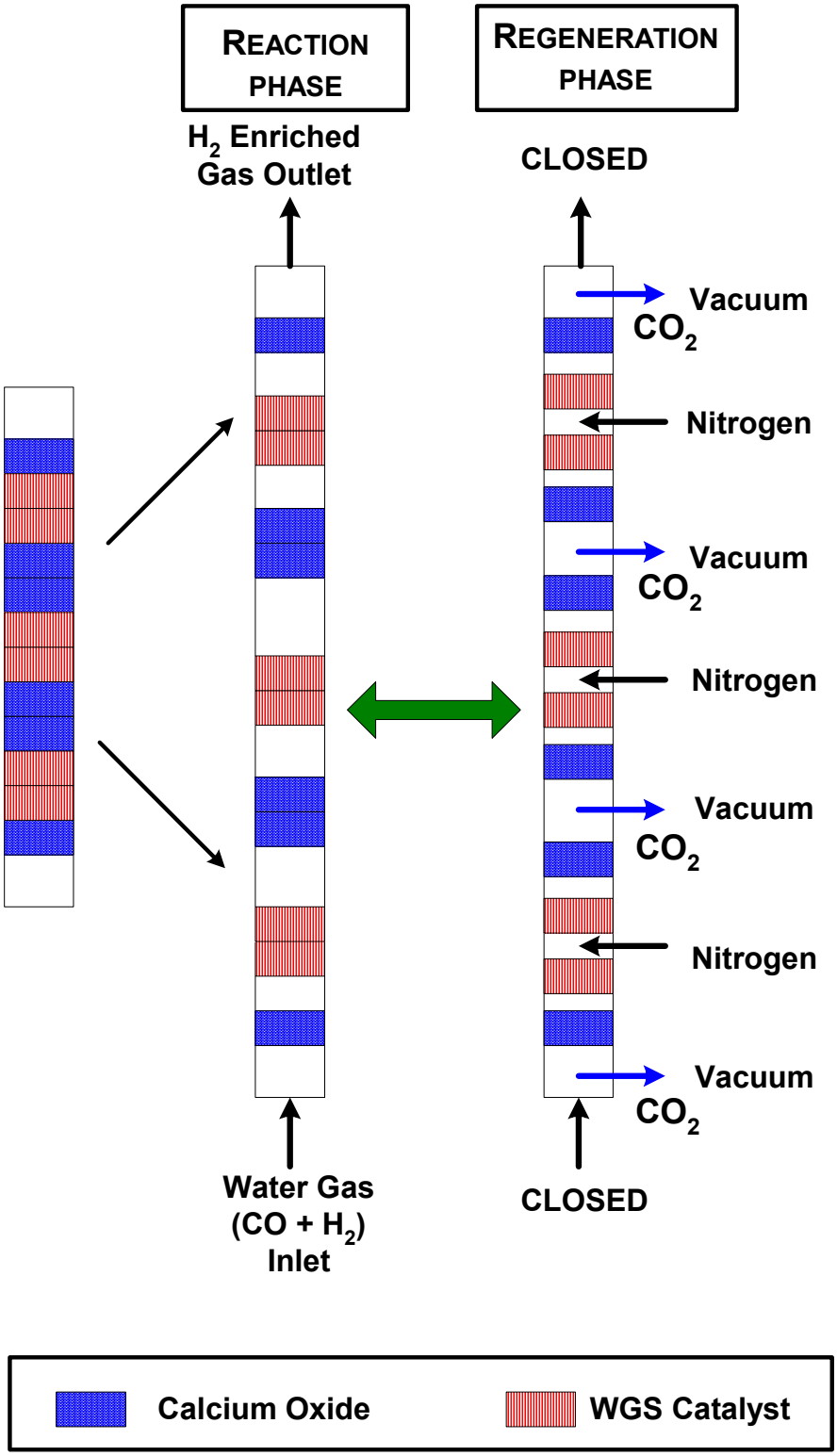


Figure 3. Schematic of novel multi-fixed-bed reactor for investigating the effect of CO_2 during regeneration on the catalyst performance.

This setup enables us to demonstrate the effect of CO_2 on catalyst activity. However, under actual operating mode, as shown in the Project Vision outlined in the Annual Technical Progress report (September 2004), the sorbent particles will be injected upstream of the WGS catalyst bed. This is an entrained flow system whereby the particles flow through the catalyst bed enhancing hydrogen production and capturing CO_2. The reacted sorbent particles are subsequently separated from the gas mixture, calcined in a separate rotary calcined and subsequently injected for carbonation. Thus, the contact between CO_2 resulting during calcination and WGS catalyst would not occur under commercial scale operation as envisioned for a coal-gasification plant. However, it is not feasible to demonstrate this under laboratory scale of operation.

Steam Calcination

Experiments were conducted to investigate the effect of steam on the calcination of precipitated calcium carbonate sorbent. The steam calcination was conducted in an integral fixed bed reactor which was described earlier in Figure 2. This was the same reactor setup that was used to investigate the simultaneous WGSR and carbonation reactions. The steam calcination was conducted in a temperature range of 700-850 ^oC with the steam composition ranging from 0-80% in the system. The other diluent gases flowing through the system were N_2 and CO_2 which served as carrier gas to enable the transport of steam into the reactor assembly. Typically about 2 grams of the sorbent was loaded in the reactor and a mixture of 80 % steam and 20 % diluent gas (N_2 or CO_2) flowed through the reactor. The effluent gas from the reactor was constantly monitored using gas analyzers for the presence of CO_2. The absence of CO_2 in the outlet gas stream ensured complete calcination of the sorbent. Finally, the calcined sorbent was analyzed for its surface properties using a Nova 2200 BET analyzer. In addition, the reactivity of this sorbent was analyzed for CO_2 capture capacity using a Perkin Elmer Thermogravimetric analyzer (model TGA 7). The sorbent was carbonated in a 10% CO_2 stream at 700 ^oC.

Chemical Analysis of Calcium Sulfide

Numerous analytical techniques including iodine-based titration were tried to accurately quantify sulfide content. However, the variability in the analytical procedure

warranted another technique for its analysis. We have eventually developed a procedure that first involves the liberation of H_2S from CaS by the addition of HCl acid. This mixture is heated in refluxing mode to ensure the completion of this reaction. The exiting gases are then sent through a gas sparger into a solution of NaOH and H_2O_2. The NaOH traps the H_2S in the form of Na_2S and the H_2O_2 stabilized it further by converting it to sulfate ions, SO_4^{2-}. The concentration of sulfate ions is estimated using an Ion Chromatography setup procured from Alltech. A mobile phase consisting of $NaHCO_3/Na_2CO_3$ provides adequate peak resolution on an Allsep 7u anionic column.

RESULTS AND DISCUSSIONS

Sub-atmospheric Calcination

Thermodynamics of sub-atmospheric Calcination

The thermodynamics of calcination, evaluated by HSC chemistry software, is represented in the form of equilibrium partial pressure of CO_2 as a function of temperature, as shown in Figure 4.

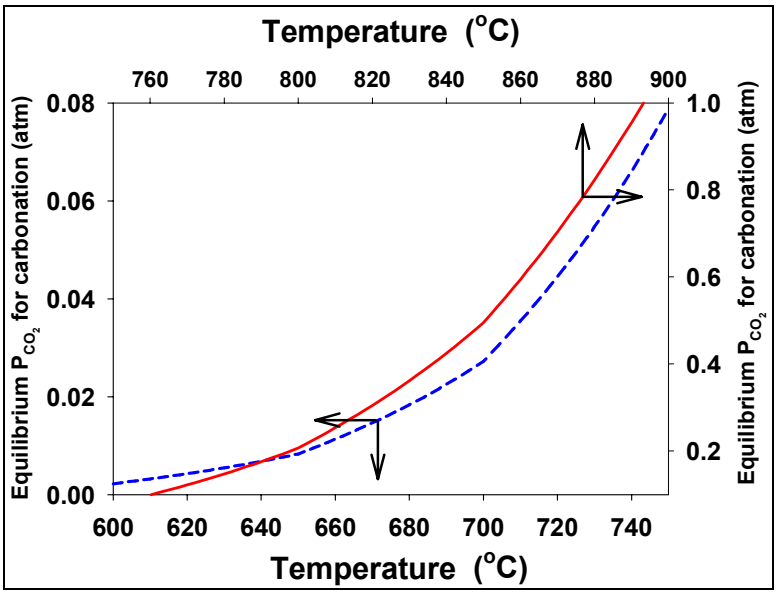


Figure 4: Equilibrium Partial Pressure of CO_2 as obtained by thermodynamics (0-1 atm)

This figure indicates that carbonation is favored under process conditions above the curve and calcination occurs at conditions below the equilibrium curve. For example, the Gibbs free energy of calcination is negative for temperatures above 890°C for a partial pressure of CO_2 (P_{CO2}) of 1 bar. It has been amply demonstrated that the ultimate CO_2

capture capacity (W) of most sorbents employed at high temperature monotonically falls with increasing number of CCR cycles (Abanades and Alvarez, 2003; Iyer et al., 2004). While numerous studies have been conducted on the carbonation reaction to detail the sorbent reactivity, kinetics, mechanism and its mathematical modeling, sufficient emphasis has not been placed on the calcination process, as it relates to this CO_2 separation process. Current calciner designs primarily involve the combustion of fuel with air inside the rotating tube to supply the sensible heat and heat of calcination directly. The exiting gases, still dominated by nitrogen, are enriched in CO_2, which is released from the calcining limestone. However, this design is not amenable to generating a pure CO_2 stream. It is thus imperative that the calcination designs and methods be optimized to maintain the sorbent structure to maximize reactivity, in a way that the purity of the eventual CO_2 stream is not compromised.

Calcination Configurations

This CCR scheme can be carried out in two modes of operation *viz.* temperature and pressure swing and any combination thereof. Calcination can be induced by either increasing the temperature of the carbonated product or by reducing the P_{CO2} in the calciner such that the process conditions fall below the thermodynamic equilibrium curve. Figure 5 shows various configurations of the calciner operation which detail the mode of heat input to the calciner. The use of air in Figure 5(a) represents direct calcination, which is representative of the commercial calcination process mentioned earlier. However, a similar reactor design can be implemented in the CCR scheme if pure oxygen is used in place of air. The fuel would then form only CO_2 and H_2O due to its combustion. The released CO_2 from reacted product and the CO_2 from the fuel combustion can now be further purified by a simple condensation and removal of steam. Depending on the fuel used for the direct calcination, other trace gases such as SOx and NOx may be emitted, necessitating further control technologies. In particular, make-up calcium would be necessary to replace the sorbent consumed by SO_2 in the calciner (Iyer et al., 2004).

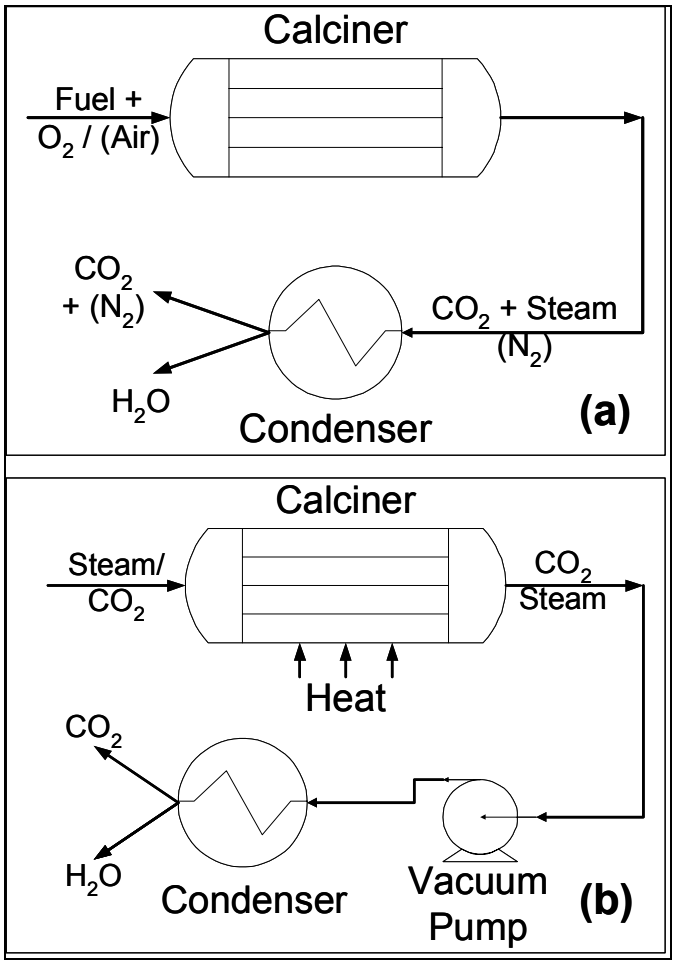


Figure 5: (a) Direct fired Calcination Configuration. (b) Indirect fired Calciner Configurations

Alternatively, in the absence of pure oxygen, the heat of calcination can be supplied indirectly as shown in Figure 5(b). The addition of heat will induce calcination, which leads to CO_2 buildup in the calciner. However, the flow of CO_2 out of the reactor is possible only if the P_{CO2} becomes greater than 1 bar. Thermodynamically, P_{CO2} becomes greater than 1 bar only above 890^{o}C. It is well known that high temperatures cause sorbent sintering, which reduces its porosity, thereby leading to a drastic reduction in reactivity. Pressure swing mode of operation enables lowering of the calcination temperature to circumvent the sintering problem. A lower P_{CO2}, required by pressure swing operation, is achieved by either dilution of evolved CO_2 or by an overall reduction in pressure of the calciner. For example, a reduction in P_{CO2} below 0.0358 bar would lower the calcination temperature to below 700^{o}C. Lowering P_{CO2} can be accomplished by flowing diluent gas through the calciner. However, only steam is an acceptable diluent gas since any other gas such as air, nitrogen, etc. will mix

with the evolved CO_2 defeating the overall objective of isolating a pure CO_2 stream. The reduction in overall calciner pressure, while maintaining 100% pure CO_2, can be achieved using a vacuum pump which removes CO_2 as it evolves from calcination.

Effect of Sorbent loading: scale-up

Extensive work has been carried out during this period on the calcination of limestone. The effect of temperature, sorbent type and level of vacuum (absolute pressure) inside the calciner on the calcination of limestone sorbent was studied previously by our research group. The earlier experiments were carried out on 0.5-2 g samples in the 700-800^oC temperature range. However, it is important to study the calcination kinetics and physical properties of the resulting CaO sorbents on larger samples in view of scale-up considerations. We have observed that heaping of $CaCO_3$ during its calcination causes sintering of the sorbent particles due to the CO_2 evolved due to the calcination of the surrounding calcium carbonate particles. Heaping also induces additional heat transfer resistances due to masking of the underlying sorbent by the exposed layers. The heat transfer limitations are greater and generally slow the kinetics of calcination as the only way to convey heat to the $CaCO_3$ is through radiation and conduction through the ceramic tube. Thus a higher calcination temperature (T=800 and 880 ^oC) is required when relatively larger quantity of sorbent is calcined.

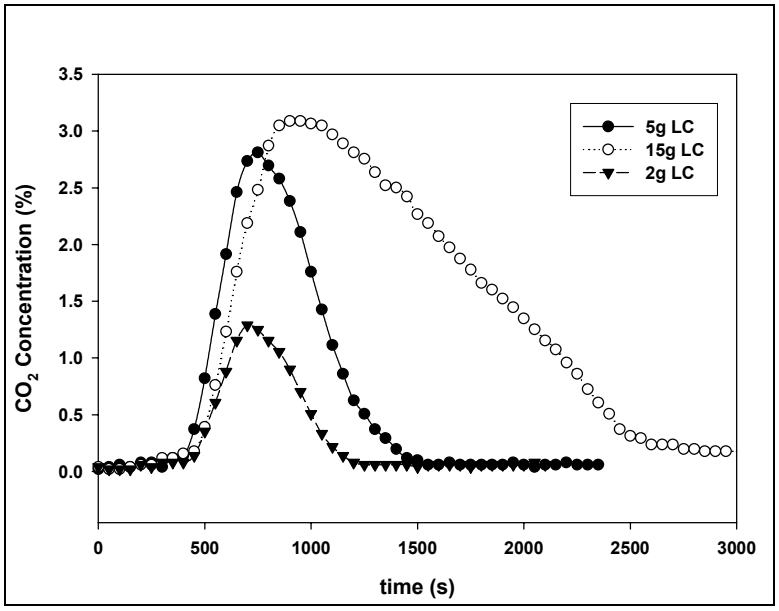


Figure 6: Effect of sorbent loading on the calcination kinetics.

We have established that heaping yields a lower surface area CaO sorbent, perhaps due to CO_2 aided sintering and the higher temperature of calcination. Figure 6 shows the effect of sorbent loading on the kinetics of the calcination of naturally occurring limestone, which we termed as Linwood Carbonate (LC). This sample was procured from Linwood Mining & Minerals Company (5401 Victoria Avenue, Davenport, IA 52807-2991). Figure 6 amply illustrates that a larger sorbent loading requires more time to calcine. While 2g sample required about 700s for 80% extent of calcination, a 15g sample required approximately three times longer residence time. The effect of heaping on heat transfer is also clearly delineated in Figure 6. We can see that it takes about 5600 seconds for the last 20% conversion when a batch of 15g sample is being calcined. This is due to the fact that the heating rate necessary for calcination of the sorbent trapped in the middle layers is not adequate enough.

Effect of Diluent Flow rate

It can be observed from Figure 6 that the calcination time required for larger samples under pure vacuum conditions is too long. However, the addition of heat to the calcining sorbent through convective means should accelerate calcination.

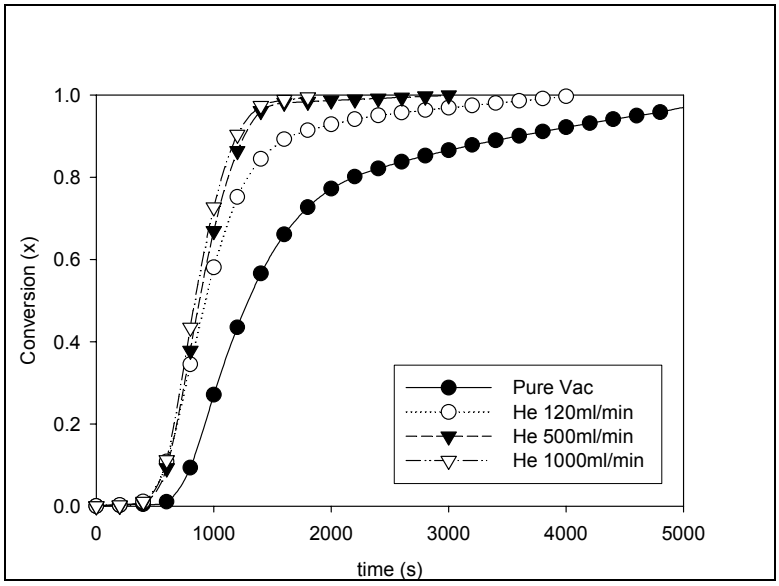


Figure 7: Effect of Diluent Flowrate (0-1000ml/min of He) -Calcination of 10g LC,28"Hg vacuum and T=880 ^{o}C

This is accomplished through the use of a pre-heated diluent gas flow over the calcining sorbent. Figure 7 shows the effect of flow rate of diluent helium gas on the calcination behavior. Figure 7 indicates that in the absence of diluent flow, we achieve only 78%

calcination in 2000s. In contrast a steady diluent flow of 120 ml/min attains ~93% in 2000s. As the diluent flow is increased to 500 ml/min, 90% calcination occurs within 1200s. It is also useful to note that an increase in diluent flow to 1000 ml/min does not decrease the heat transfer resistance significantly.

Effect of Diluent Type

Calcination experiments were conducted in the presence of different diluent gas types. This is to establish qualitatively the influence of thermal properties (thermal conductivity, heat capacity) of the diluent gas on the heat transfer properties, and thereby its influence on the calcination rate. For example, at 1000K the thermal conductivity of He (0.354 W/m.K) is higher than that of N_2 (0.0647 W/m.K), which could lead to a difference in the calcination rate (Perry and Chilton, 1998). Figure 8 indicates the influence of helium, nitrogen and argon on the calcination of 10g samples of Linwood carbonate. It can be observed from Figure 8 that helium indeed causes a faster calcination.

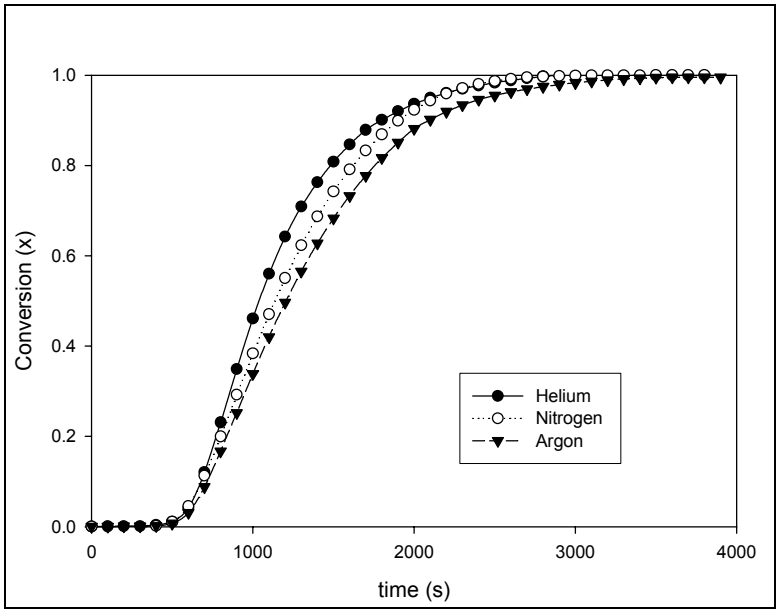


Figure 8: Choice of Diluent Gas (He/N2/Ar) - Calcination of 10g LC at 28”Hg vacuum T=880 ^{o}C.

In a commercial operation, we cannot use these particular gases because the gas mixture exiting the calciner will consist of CO_2, which is evolved from the calcination process and these diluent gases, thereby defeating the overall purpose of isolating a pure CO_2 stream. However, these experiments lay a foundation for the use of higher thermal conductivity gases

such as steam (0.0978 W/m.K). Steam has the added advantage of ease of separation from steam/CO_2 mixtures by its removal by condensation.

Steam Calcination

The samples were steam calcined at 700, 800, and 850 ^oC in a gas mixture of 80 % steam and 20 % N_2. In addition, for each of these temperatures the samples were also calcined in a pure N_2 stream as a control run for comparison purposes. This was to determine the effect of steam on the calcination process in comparison to air-calcination which is commonly practiced. However, calcination in air would defeat the entire objective of producing a sequestration ready CO_2 stream as discussed in earlier reports (March 2005). Hence steam and other alternatives are being evaluated for calcination of the carbonated sample.

The first set of experiments that was conducted compares the subsequent reactivity of the calcined sorbent calcined at 700 ^oC. The samples were calcined in (a) pure N_2 stream and (b) 80%-20% steam-N_2 mixture. As shown in Figure 9, the CaO sorbent calcined in pure N_2 exhibits a higher maximum CO_2 weight percent capture (65%) than CaO calcined in an 80% steam-20% N_2 mixture (60%). The CaO sorbent calcined in pure N_2 reaches its maximum capture capacity in a shorter amount of time (20 minutes) than the CaO sorbent calcined in the 80% steam-20% gas mixture (30 minutes).

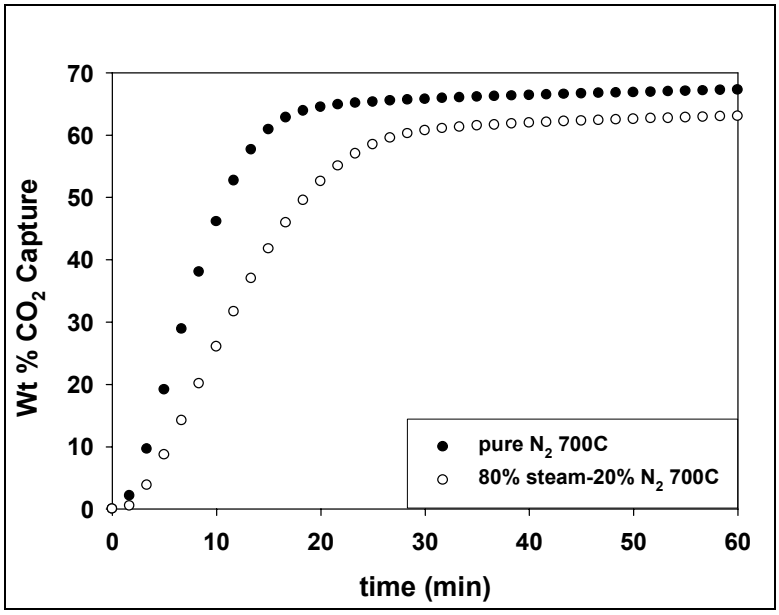


Figure 9. Comparison of the PCC sorbent reactivity calcination at 700ºC in pure N_2 and a 80-20% steam-N_2 mixture.

Another set of experiments performed compares the reactivity of CaO following calcination at 800-820ºC as shown in Figure 10. The $CaCO_3$ was calcined into CaO under the following conditions at 800 ^oC: (a) pure N_2 stream (b) 80% steam-20% N_2 mixture, and (c) 80% steam-20% CO_2 mixture at 820ºC. The steam calcination run of 80% steam-20% CO_2 mixture was performed at 820ºC because at 800ºC, calcination will not occur due to thermodynamic equilibrium limitations. As shown in Figure 10, CaO sorbent calcined in pure N_2 has the highest CO_2 weight % capture (65%), followed by the CaO sorbent calcined in 80% steam-20% N_2 (58 wt% capture). The CaO sorbent calcined in 80% steam-20% CO_2 mixture has a capture capacity of only 50%. It appears that all three CaO sorbents reached its maximum CO_2 weight percent capacity at the same time of 30 minutes from the start of carbonation.

Figure 11 shows the reactivity of CaO sorbent calcined under the following conditions at 850ºC (a) pure N_2 (b) 80% steam-20% N_2 mixture (c) 80% steam-20% CO_2 mixture. The reactivity of the calcined CaO sorbent for each case is almost identical up to 25 minutes of carbonation (43 - 47 wt% capture). After 25 minutes, the common trend of maximum CO_2 capture capacity is seen with the most reactive CaO sorbent being that of pure N_2 calcination (60 wt% capture) and the steam-CO_2 calcination resulting in 60 wt% capture.

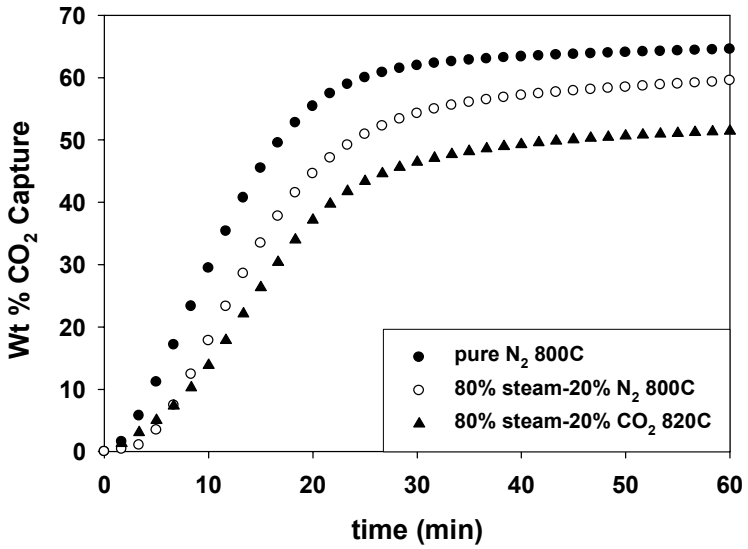


Figure 10. Comparison of the PCC sorbent reactivity calcination (a) pure N_2 at 800ºC (b) 80-20% steam-N_2 mixture at 800ºC and (c) 80-20% steam-CO_2 mixture at 820ºC.

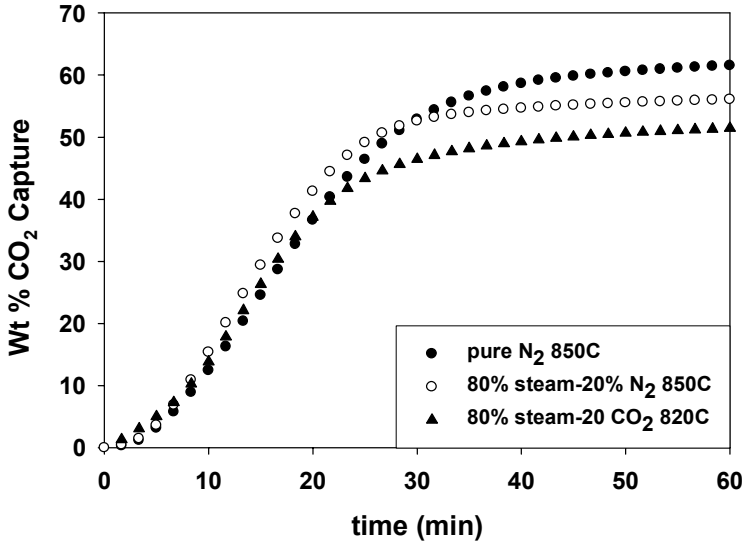


Figure 11. Reactivity of Calcined Sorbent after Calcination at 850ºC (a) pure N_2 (b) 80-20% steam-N_2 mixture and (c) 80-20% steam-CO_2 mixture.

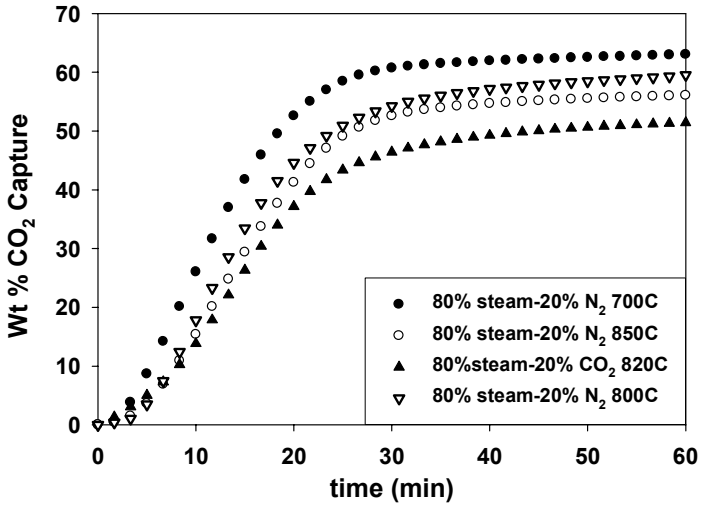


Figure 12. Reactivity of Calcined Sorbent after Steam Calcination at various temperatures using CO_2 and N_2 as the carrier gas.

A comparison of the steam calcination runs at different temperature ranges is presented in Figure 12. It is shown in the figure that the wt% CO_2 capture of the steam-N_2 calcined sorbent changes with reaction temperature and the carrier gas type. The wt% capture capacity of the 80% steam-20% N_2 calcined sample increases from 52 wt% capture at 850 ^oC to 55 wt% capture at 800 ^oC and finally 60 wt% capture at 700 ^oC. For the samples calcined using

the 80% steam-20% CO_2 stream the wt% CO_2 capture , and the rate of carbonation are higher using CaO sorbent calcined at lower steam calcination temperatures.

The surface area and the pore volume of the calcined CaO sorbent are presented in Table 1. The CaO sorbent that has the highest surface area and pore volume is the result of calcination in an 80% steam-20% N_2 stream at 700ºC. At temperatures of 700ºC and 800ºC, calcination of the sorbent with steam results in a CaO sorbent with a higher sorbent surface area and pore volume than calcination in 100% N_2. This is evident from Table 1 below.

Table 1. Morphological properties of CaO Sorbent following calcination

Calcination Gas	Temp (ºC)	SA (m^2/g)	Pore Vol (cc/g)
100% N_2	700	11.86	0.03526
100% N_2	800	7.96	0.01998
80% Steam-20% N_2	700	13.55	0.06781
80% Steam-20% N_2	800	9.86	0.02155
80% Steam-20% CO_2	820	9.42	0.03905

CaS Carbonation in the liquid phase

X-ray Diffraction analysis

It was difficult to evolve H_2S by heating a solution of CaS in water, even to boiling. Figure 13 shows the XRD analysis of the product that was obtained after drying. A similar trend in crystal structure was observed in the product obtained even when helium is bubbled through aqueous CaS slurry. The effect of CO_2 gas was studied subsequently. Aqueous slurry is made by mixing 1 gram of CaS in 250 ml of water. Pure CO_2 gas is then bubbled through the slurry containing 1 gram of CaS in 250 mL water as it passes through the fritted quartz distributor. The solid product is filtered and dried in a vacuum oven before subjecting it to various physical and chemical characterizations. Figures 14 (a) and (b) reveal the XRD patterns of the solid after 10 and 60 minutes of carbonation. It can be seen that the peaks have significantly shifted away from the CaS structure, signifying the occurrence of the carbonation reaction.

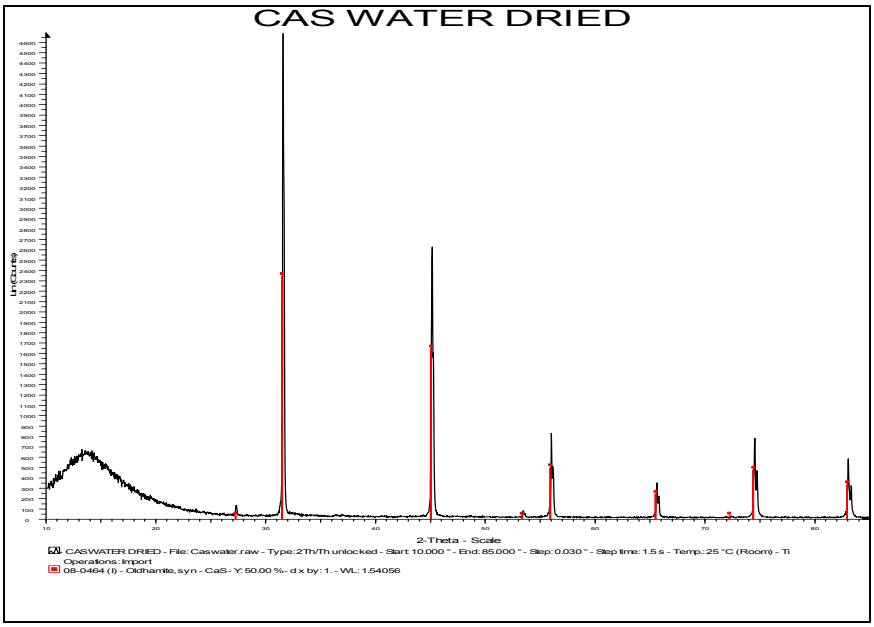
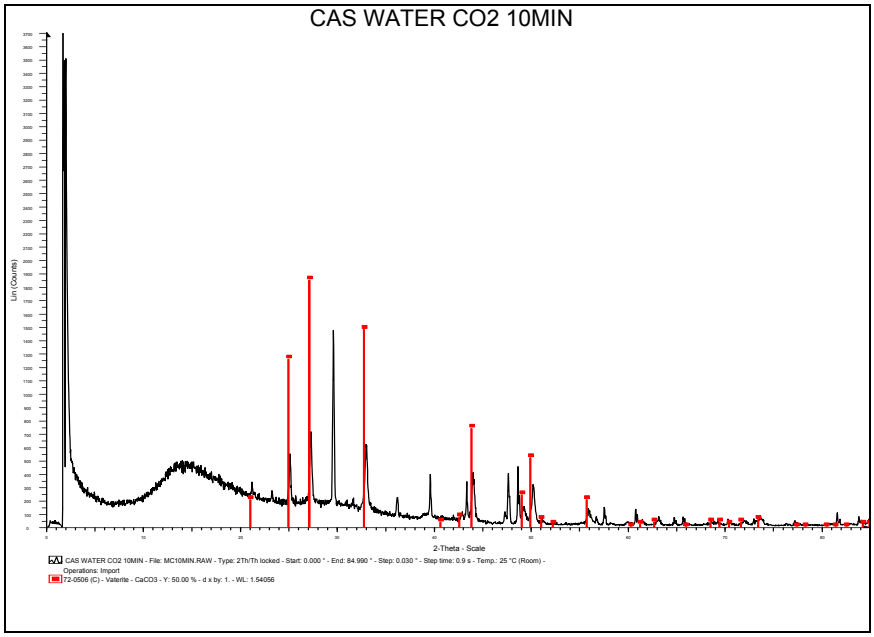
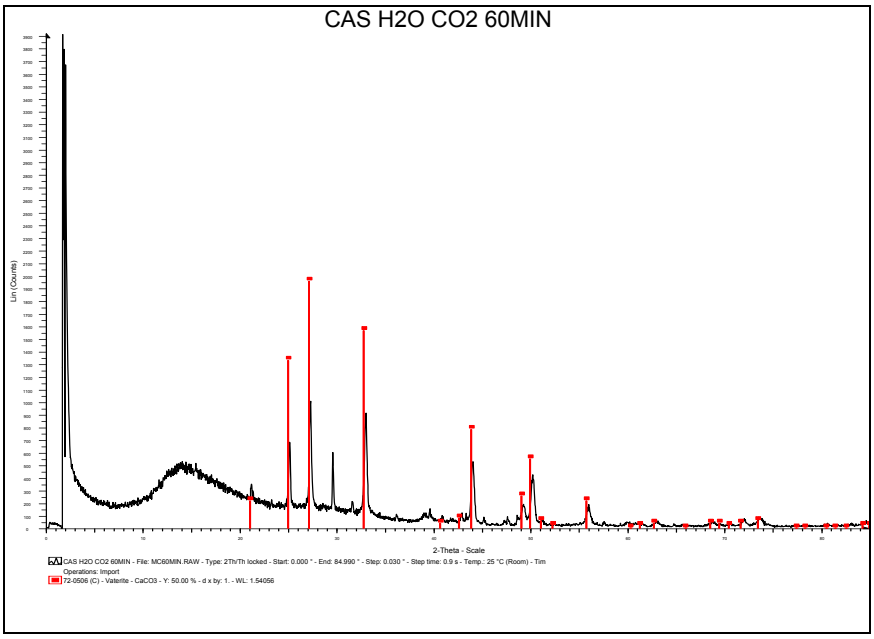


Figure 13: XRD analysis showing CaS in the dried product after heating CaS in water



(a) 10 minutes



(b) 60 minutes

Figure 14: XRD patterns showing presence of *$CaCO_3$* after bubbling CO_2 in CaS-water slurry

Preliminary experiments were carried out to understand the effect of N40V dispersant concentration on the structural characterization of the $CaCO_3$ formed by this carbonation reaction. This dispersant is used in the synthesis of the high reactivity mesoporous PCC sorbent (Agnihotri et al., 1999). In the absence of N40V, the BET surface area (SA) and pore volume (PV) values were 9.28 m^2/g and 0.02447 cc/g respectively. When the CaS/N40V weight ratio is altered to 40, we observed a decrease in SA to 2.36 m^2/g, but an increase in PV to 0.08276 cc/g. It can be seen that the introduction of N40V increases the total PV in the sorbent, which is useful in enhancing its reactivity towards sulfidation reactions.

Hydrogen production by simultaneous Carbonation and WGSR

Analysis of the Gas Composition during Combined Reactions

Figures 15-19 show the analysis of the gas composition exiting the combined WGS-carbonator reaction. The experiments were performed at 600 ^oC with an inlet gas composition of 10.3% CO, 31% H_2O with the balance being N_2. The total gas flow rate was kept at 0.725 slpm. While 0.25 g of HTS was loaded in each case the amount of calcined (PCC-CaO or LC-CaO) loaded was about 1.77g. The gas exiting the reactor typically

consists of CO, H_2, CO_2, H_2O and N_2. However in a real fuel gas system the dilution N_2 will not be present. Hence, the calculations for N_2 free gas compositions were performed and Figure 15 shows the N_2 free gas compositions.

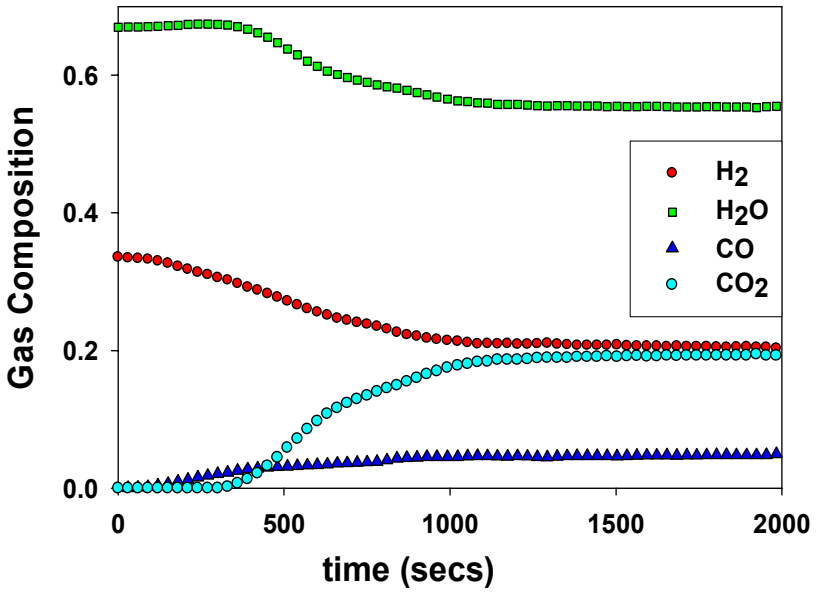


Figure 15: Real time nitrogen free gas composition of the reactor system during the combined WGS- carbonation reaction using PCC-HTS system (T = 600 ^oC, 10.3% CO, 31% H_2O, Total flow = 0.725 slpm).

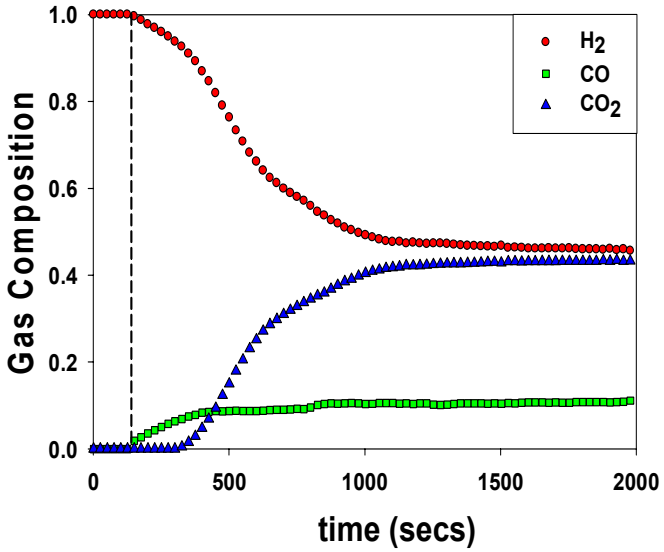


Figure 16: Real time nitrogen and steam free gas composition of the reactor system during the combined WGS-carbonation reaction using PCC-HTS system (T = 600 ^oC, 10.3% CO, 31% H_2O, Total flow = 0.725 slpm).

It is evident from Figure 15 that as the breakthrough curve is obtained with increasing time, the H_2 concentration decreases while the CO and CO_2 concentration increases. The steam molar flow rate remains fairly constant but its composition seems to decrease due to the total increase in the number of moles of CO and CO_2 in the reactor outlet. However, in an actual system steam will be condensed from the reactor outlet and hence the resultant gas stream will comprise of only CO, H_2, and CO_2. Hence steam as well as N_2 free gas composition analyses were calculated. Figure 16 shows the gas composition for a PCC-HTS system while Figure 17 shows that for a LC-HTS system. From Figure 16 it is evident that 100% pure hydrogen stream is obtained for 139 seconds for the PCC system. For that time period the CO as well as the CO_2 concentration in the gas stream is negligible. Beyond that time the CO concentration gradually increases and reaches the steady state value. Similarly, the H_2 composition decreases while the CO_2 composition increases with reaction time and they approach the corresponding steady state value. Figure 17 shows similar trends with respect to LC-HTS system.

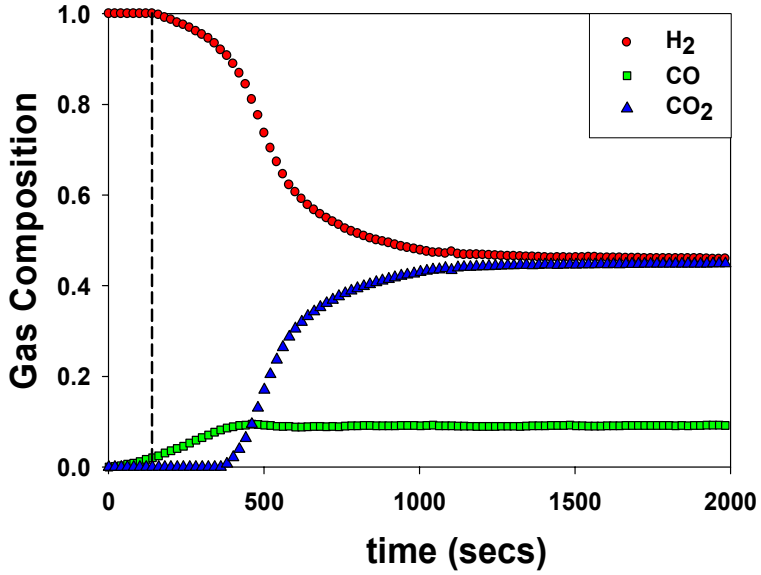


Figure 17: Real time nitrogen and steam free gas composition of the reactor system during the combined WGS-carbonation reaction using LC-HTS system (T = 600 ^oC, 10.3% CO, 31% H_2O, Total flow = 0.725 slpm).

Figure 18 shows the shows the comparative analyses of the H_2 gas composition for PCC and LC system. It is evident from the figure that the PCC system demonstrates higher H_2 concentration in the gas stream as compared to LC system. Similarly, Figure 19 shows that the CO_2 composition in the gas stream is higher for LC than PCC. Thus, these plots

corroborate the superior performance of the PCC sorbent over the naturally occurring sorbents.

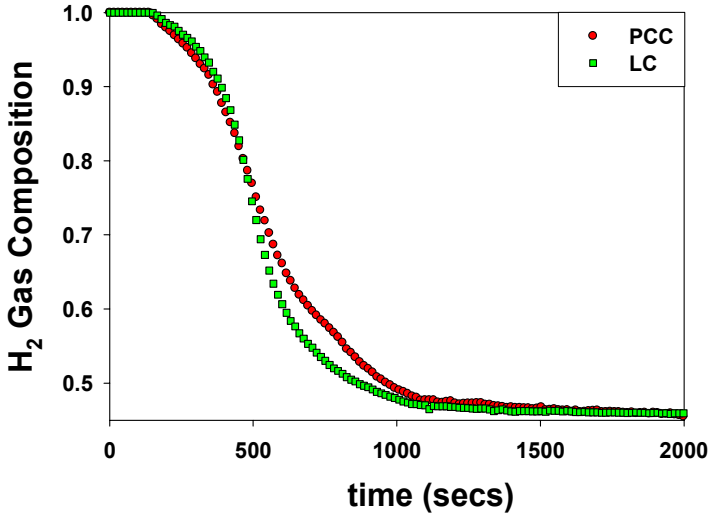


Figure 18: Comparison of real time nitrogen and steam free H_2 gas composition system during the combined WGS-carbonation reaction using PCC-HTS and LC-HTS systems (T = 600 ^oC, 10.3% CO, 31% H_2O, Total flow = 0.725 slpm).

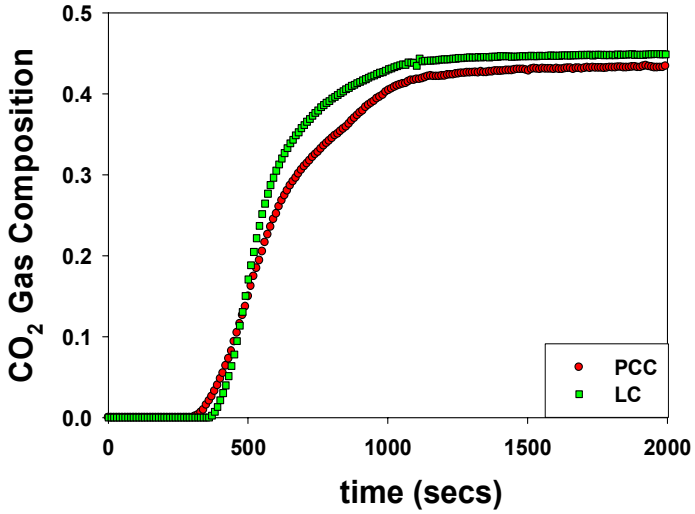


Figure 19: Comparison of real time nitrogen and steam free H_2 gas composition system during the combined WGS-carbonation reaction using PCC-HTS and LC-HTS systems (T = 600 ^oC, 10.3% CO, 31% H_2O, Total flow = 0.725 slpm).

Calculation procedure for simultaneous WGS-Carbonation reactions

In the combined WGS-carbonation reaction scheme, described earlier, we have CO, N_2 and H_2O entering the reactor system. The mass flows of these inlet streams are known. From these gases, CO and H_2O get consumed but N_2 remains the same. However, at the outlet of the reactor only the gas compositions are known which are measured by CO, CO_2 and H_2 analyzers. Hence, a detailed calculation procedure to compute the CO conversion from the % gas composition is outlined below.

$$\%CO_{out} = \frac{n_{CO_{out}}}{n_{T_{out}}} = \frac{n_{CO_{out}}}{n_{CO_{out}} + n_{N_2} + n_{H_{2out}} + n_{CO_{2out}}} \qquad \text{----------(a)}$$

Rearranging:

$$\%CO_{out} \quad \left(n_{N_2} + n_{H_{2out}} + n_{CO_{2out}}\right) = n_{CO_{out}} \quad \left(1 - \%CO_{out}\right)$$

$$n_{CO_{out}} = \frac{\left(n_{N_2} + n_{H_{2out}} + n_{CO_{2out}}\right) \quad \left(\%CO_{out}\right)}{\left(1 - \%CO_{out}\right)} \qquad \text{----------(b)}$$

Similarly,

$$\%CO_{2out} = \frac{n_{CO_{2out}}}{n_{T_{out}}} = \frac{n_{CO_{2out}}}{n_{CO_{out}} + n_{N_2} + n_{H_{2out}} + n_{CO_{2out}}} \qquad \text{----------(c)}$$

Rearranging:

$$\%CO_{2out} \quad \left(n_{N_2} + n_{H_{2out}} + n_{CO_{out}}\right) = n_{CO_{2out}} \quad \left(1 - \%CO_{2out}\right)$$

$$n_{CO_{2out}} = \frac{\left(n_{N_2} + n_{H_{2out}} + n_{CO_{out}}\right) \quad \left(\%CO_{2out}\right)}{\left(1 - \%CO_{2out}\right)} \qquad \text{----------(d)}$$

Since $n_{H_{2out}}$ is not known,

$$n_{H_{2out}} = n_{CO_{in}} - n_{CO_{out}} \qquad \text{----------(e)}$$

Substituting (e) in (d) :

$$n_{CO_{2out}} = \frac{\left(n_{N_2} + n_{CO_{in}}\right) \quad \left(\%CO_{2out}\right)}{\left(1 - \%CO_{2out}\right)} \qquad \text{----------(f)}$$

Substituting (6) in (2):

$$n_{CO_{out}} = \frac{\left(n_{N_2} + n_{CO_{in}} - n_{CO_{2out}} + n_{CO_{2out}}\right) \quad \left(\%CO_{out}\right)}{\left(1 - \%CO_{out}\right)}$$

Simplifying,

$$n_{CO_{out}} = \frac{\left(n_{N_2} + n_{CO_{in}}\right) \quad \left(\%CO_{out}\right)}{\left(1 - \%CO_{2out}\right)} \qquad \text{----------(g)}$$

where,

$n_{N_{2in}} = n_{N_{2out}} = n_{N_2}$ = molar flow rate of nitrogen in the analyzer

$n_{CO_{in}}$ = molar flow rate of CO into the reactor system

$n_{CO_{out}}$ = molar flow rate of CO out of the reactor system

$n_{CO_{2out}}$ = molar flow rate of CO_2 out of the reactor system

$n_{H_{2out}}$ = molar flow rate of H_2 out of the reactor system

$\%CO_{2out}$ = Percentage of CO_2 in the outlet stream from the analyzer

$\%CO_{out}$ = Percentage of CO in the outlet stream from the analyzer

Thus eqn (g) gives the molar flow rate of CO out of the system from which the CO conversion can be easily computed.

CONCLUSIONS

The enhanced water gas shift and carbonation reaction was investigated at 600^{o}C and ambient pressures with a steam:CO ratio of 3:1. The PCC sorbent shows superior performance over the commercial LC sorbent as demonstrated by the CO conversion breakthrough curves as well as the H_2 gas formation analyses. Gas composition analyses (steam and N_2 free) show the formation of 100% pure hydrogen during the first 139 seconds

for the PCC system. Sub-atmospheric calcination studies reveal the effect of vacuum level, diluent gas flow rate, thermal properties of the diluent gas and the sorbent loading on the calcination kinetics which play an important role on the sorbent morphology. Lowering vacuum levels, reducing sorbent loading and increasing diluent gas flow rates augments the calcination rate and the mass/heat transfer rates. Steam calcination studies at 700-850 ^{o}C reveal improved sorbent morphology over regular N_2 calcination. A mixture of 80% steam and 20% CO_2 at ambient pressure was used to calcine the spent sorbent at 820 ^{o}C thus lowering the calcination temperature. However, the reactivity of the steam-calcined sorbent is poor compared to the N_2 calcined samples. Regeneration of calcium sulfide to calcium carbonate was achieved by carbonating the calcium sulfide slurry by bubbling CO_2 gas at room temperature. Addition of anionic dispersant, while regenerating calcium sulfide increases the sorbent morphology (surface area and pore volume) leading to improved sorbent reactivity.

Current Status of the Project and Future Approach

The high temperature and high pressure magnetic suspension balance was procured from VTI corporation and was installed in July-Aug 2005. The fixed-integral bed reactor setup was suitably modified with appropriate gas analyzers and the combined experiments were conducted that demonstrated pure hydrogen formation at ambient pressures. Future investigations are focused on conducting multicyclic experiments with in-situ WGSR/carbonation and calcination cycles. The reactor system will be configured to operate at high pressures (0-20 bar) while conducting the high pressure combined WGS-carbonation experiments. The possibility of reducing steam:CO ratio will be also investigated.

Conference Presentations

This project has resulted in following conference papers/presentation during the reporting period.

- Iyer, M.V.; Gupta, H; Sakadjian, B.B.; and Fan, L.-S. “Enhancing Hydrogen Production With In-Situ CO_2 Separation Using CaO/Catalyst Systems” AIChE Annual Tech. Meeting, Austin, TX, (November **2004**).

- Gupta, H; Iyer, M.V.; Sakadjian, B.B.; and Fan, L.-S., "The Role of CaO in Maximizing Hydrogen Production from Fossil Fuels" Proc. Fuel Cell Seminar, San Antonio, TX, November **2004**.
- Iyer M.V., Gupta H., Sakadjian B. S. and Fan L.-S. "High temperature CO_2 capture and hydrogen production using calcium oxide: Process development and economics for combustion and gasification systems" *Proc. 30th Int.Tech.Conf.Coal Utilization & Fuel Systems*, ***30(1)***, 419-426 (April **2005**).

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